Diagnosis of a hydrogen/air fuel cell by a statistical model-based method

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Abstract: This paper proposes a diagnosis method of a hydrogen/air fuel cell using a quasi-static model coupled to a parameter identification method that are both described. An original statistical approach is proposed in an effort to obtain a certain guaranty on the validity of the identified parameters and raise in this way the associated "confidence index". The analysis of the degradation of a fuel cell is afterwards achieved by comparing parameters identified before and after the degradation. A diagnosis is then presented based on the analysis of the different losses occurring within the fuel cell in an effort to monitor and control on-board systems.

Keywords: H_2/Air Fuel cell, diagnosis, statistics, modeling, crossover current, least square algorithm, state of health

I. INTRODUCTION

We find ourselves at the edge of an energetic mutation. Indeed, we are getting closer to the exhaustion of fossil fuel resources coupled to environmental problems such as the greenhouse effect or nuclear wastes handling. We must find different energy sources and it seems that there are no perfect solutions but rather a large number of alternatives.

Hydrogen (H_2) has probably a role to play in the future energy context. However, as it does not exist in nature, hydrogen has to be synthesized, ideally from renewable energy sources (solar panels, wind turbines…). These technologies produce energy randomly (dependent on the weather) but production could be smooth out by a hydrogen storage system. Thus, electrolysers and fuel cells (FC) appear to be an interesting alternative.

A fuel cell is composed of several monocells where each monocell undergo a redox reaction. Using platinum as a catalyst, hydrogen and oxygen react to produce water, electricity and heat according to the following global reaction:

$$H_2 + \frac{1}{2} 0_2 \rightarrow H_2O + electricit\ \ y + heat \qquad (1)$$

Figure 1 introduces the schematic of a Proton Exchange Membrane Fuel Cell or PEMFC.

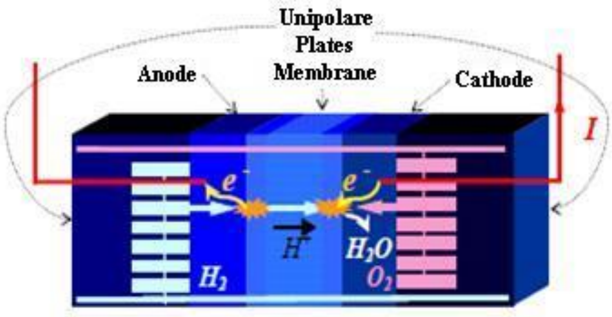

Figure 1: PEMFC schematic

The LAPLACE laboratory has mainly focused its research on low temperature PEM fuel cells, a technology that is close to commercialization. Parts of previous researches achieved at the LAPLACE on H_2/O_2 FC [1] [2] have been applied to H_2/Air FC for this study to establish a diagnosis of the state of health of a fuel cell.

Today, fuel cell technology is not sufficiently developed to provide energy at competitive costs and additional studies are needed to optimize its performance. In addition, monitoring approaches are also investigated to improve the reliability and life time of an embedded system. For example in electrical vehicle, the FC is submitted to strong constrain such as vibrations, temperature variations, humidity, transient regimes… These constrains have a strong impact on the FC performances, therefore, it is necessary to have feedback on the FC state of health to adapt the control and prevent damaging operation conditions.

In order to fulfill these goals, friendly representative fuel cells models are developed (circuit-based) that provide an easy approach and a quick understanding of involved physicochemical phenomenon and offer a diagnosis [1] [2] [3].

A circuit based model represents, by analogy, and through the association of electrical components, the different physical phenomena occurring inside the fuel cell, namely the different losses [2]. It has been decided that a similar circuit based model approach will be used to identify the different losses peculiar to the PEMFC (activation, diffusion, membrane resistance) in an effort to establish a diagnosis throughout physical parameters analysis.

In this article, we will first introduce our model and the parameters identification approach. The statistical method is then presented and described to move on to the application of these methods on healthy and degraded PEMFC data in a diagnosis effort.

II. Model and parameters identification method

A. *Quasi-static model*

The quasi-static circuit-based model is as following:

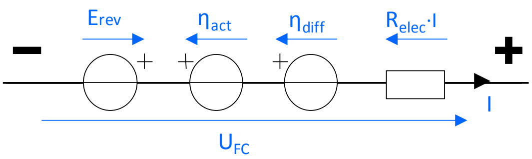

Figure 2: Quasi-static circuit-based model

We have E_{rev}: Nernst voltage

η_{act}: Activation losses

η_{diff}: Diffusion losses

R_{elec}: Ohmic losses

The theoretical voltage is represented by a voltage source as well as activation and diffusion losses (activation and diffusion losses become voltage-driven current sources in a dynamic model [6]). Ohmic losses are modeled by a resistance as it was measured to be a constant value (resistance monitoring for every point of the quasi-static curve). Therefore, we can deduce from figure 2 the overall equation of the quasi-static model (2):

$$U_{FC} = E_{rev} - \eta_{act} - \eta_{diff} - R_{elec}I \qquad (2)$$

Equation (2) can be rewritten as following (3):

$$U_{FC} = E_{rev} - \frac{RT}{\alpha nF}\ln\left(\frac{I}{I_o}\right) - (R_{elec} + R_{diff})I \qquad (3)$$

Where: α: Activation coefficient
I_0: Activation current (A/cm²)
R_{diff}: Diffusion pseudo-resistor (Ω)
R_{elec}: Ohmic losses (Ω)
R: Perfect gas constant (8.314 $J.K^{-1}.mol^{-1}$)
T: Temperature (K)
n = 2 (mol)
F: Faraday constant (96485 $C.mol^{-1}$)

Equation (3) is only true if $I >> I_0$ and if $I << I_{lim}$ with I_{lim} the limit current for gas diffusion. This last condition allowed us to linearise the diffusion losses:

$$\eta_{diff} = \left|\frac{RT}{\beta nF}\ln\left(1 - \frac{I}{I_{lim}}\right)\right| \underset{I \ll I_{lim}}{\approx} \frac{RT}{\beta nFI_{lim}} I = R_{diff}\, I \qquad (4)$$

Where β is a coefficient that takes into account every loss liked to diffusion. If I = 0 we should theoretically obtain $U_{FC} = E_{rev}$. This result cannot be obtained with equation (3). We then have a validity problem of the $U_{FC}(I)$ law on the [0;"$I>>I_0$"] interval. In addition, in the real world, the zero-current voltage is different from E_{rev} due to parasitic reactions mainly caused by hydrogen crossover throughout the membrane [4] [5]. For both previous reasons, an additional parameter I_n, a leakage current, is introduced into the overall equation (3):

$$U_{FC} = E_{rev} - \frac{RT}{\alpha nF}\ln\left(\frac{I + I_n}{I_o}\right) - (R_{elec} + R_{diff})I \qquad (5)$$

This equation governing the quasi-static behavior of a fuel cell holds four unknown parameters: α, I_0, I_n and R_{diff} that we need to determine for a diagnosis purpose. To do so, a parameters identification method is used (for the determination of R_{elec} see [2]).

B. Parameters identification method

In order to obtain the values of the four unknown parameters, a parameters extraction algorithm is used. This algorithm, described in the flowchart in Figure 3, needs experimental data to proceed. Data acquisition is done using a current sweep method [6] where *v(t)* and *i(t)* are recorded and filtered before optimization. Random initial values are fed to the algorithm along with the membrane resistance value for optimization.

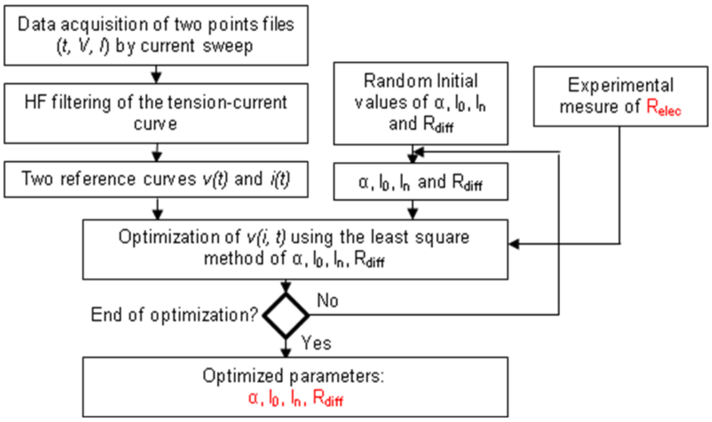

Figure 3: Flowchart of the parameters extraction algorithm

The algorithm is an optimization MATLAB function called lsqnonlin using the Levenberg-Marquardt algorithm. This iterative algorithm solves non-linear optimization problems by the least square method (parameters being non-linear with respect to the model). It is used here for the finding of a vector of parameters θ which minimize the quadratic difference between experimental data (*v(i)* curve) and a mathematical model supposed to fit to these data. Thus, the criterion to minimize is expressed by:

$$J = \sum_{i=1}^{N} V_{\exp} - V_{model}{}^{2} \qquad (6)$$

Where: V_{exp}: Experimental voltage (V)
V_{model}: Voltage calculated by the model (V)

The Levenberg-Marquardt algorithm evolves following equation (7):

$$\theta_{i+1} = \theta_i - [J_i'' + \mu[I]]^{-1} J_i' \qquad (7)$$

With: θ_i: the parameter to optimize
I: the diagonal unit matrix
J': the Jacobi
J'': the Hessian
μ_i: a strictly positive coefficient that orientates the research of the minimum value of J

The Levenberg-Marquardt was used here over other optimization algorithms (Newton-Gauss, Gradient descent and other gradient based algorithms) because its convergence rate is better when being away or close to the solution and due to its robustness [7].

C. Healthy and degraded fuel cell data comparison

The fuel cell used is composed of three cells associated in series also called a stack. It is a ZSW fuel cell, presented in figure 4 that has an active area of 100 cm² and a current density of 1A/cm².

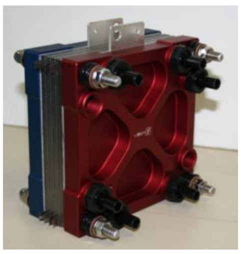

Figure 4: ZSW stack

This FC, during an ageing procedure, underwent a serious degradation due to the improper activation of a security system. Fortunately, data acquisition has been made before the incident which gave us healthy and degraded data to compare and analyze (data acquisition has been made at a temperature of 54°C). This is a perfect case for the test of our algorithm and from a diagnosis point of view.

III. Statistical approach

A. Initial parameters and number of optimization

To begin with, as we can see in figure 3, random initial values are fed to the optimization algorithm. Parameters are initially set to experimentally known values. In an effort to test the robustness of the algorithm, a random set of parameters a 100% away from initial values is imposed to the algorithm.
The statistical approach is based on a large number of optimizations. Indeed, a 100 optimizations are launched which give us a 100 vectors of optimized parameters (for each optimization a new set of initial parameters is selected by chance). These 100 vectors of parameters need to be analyzed and a final set need to be kept as the set of parameter describing the most accurately the fuel cell behavior.

B. Set of Parameters selection

Two approaches are used for the analysis of the obtained vectors of parameters. The first one, called the "minimum error method" consists in keeping the set of parameters having the lowest point-to-point error compared to experimental data (8):

$$Error = \frac{\left|V_{\exp} - V_{\mathrm{mod}\,el}\right|}{V_{\exp}}.100 \quad (8)$$

This method of parameters selection is the method usually used in the literature but the confidence index is quite low as only one set of parameters over a 100 is chosen. We can imagine that the algorithm stopped on a singularity or that several set of parameters led to the same model behavior. An additional method of selection is then developed based on the analysis of the 100 sets of parameters.

This method, that we will call the "occurrence number method", extracts the value of each parameter that is the most occurring over the 100 optimizations. Each parameter value for each optimization is inserted into a bar graph, the interval containing the most occurring value is extracted and a vector of parameter is built.

This method, despite the fact that it is, in theory, less accurate than the previous one, gives us interesting information regarding the validity of the set of parameters found by the minimum error method. Indeed, once coupled, these two methods give us a guaranty regarding the relevance of the results and increase the confidence we have in our findings.
We will now apply the presented material to healthy and degraded fuel cell data.

IV. Application to a healthy fuel cell

The quasi-static curve presented in figure 5 is the result of the parameters identification algorithm using the minimum error method. Results are brought back to the Equivalent Mean Cell (EMC). Let us note that the healthy stack membrane resistance value is $R_{elec\_healthy}=0.0012\Omega$ determined, once again, as described in [2].

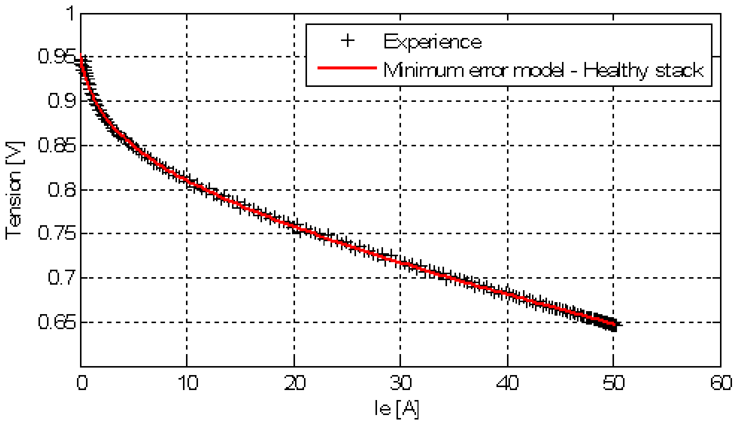

Figure 5: Quasi-static graph (EMC) – Healthy fuel cell

The table 1 presents the parameter identification results for the four unknown parameters of the quasi-static model. The two selection methods are used and we can see that either of the two methods gives the same result.

	α	I_n	I_0	R_{diff}
Min error	0.3392	0.5713	0.001907	0.001209
Max occ.	0.3392	0.5713	0.001907	0.001209

Table 1: Quasi-static identification - Healthy fuel cell

Figure 6, 7, 8 and 9 present respectively the distribution, over the 100 optimizations, of the α, I_0, I_n and R_{diff} parameters. The parameter value is extracted by taking the median value of the Δx interval containing the largest number of values. Thus this extraction method induces an error as the exact value itself is not taken.

Despite the fact that an error is introduced we can see that, for the four parameters, the algorithm find the same value for 95% of the achieved optimizations. Results being identical, regardless of the parameter selection method used, allow us to be confident in our findings. The coupling of the two different methods raises the confidence index regarding parameters identification.

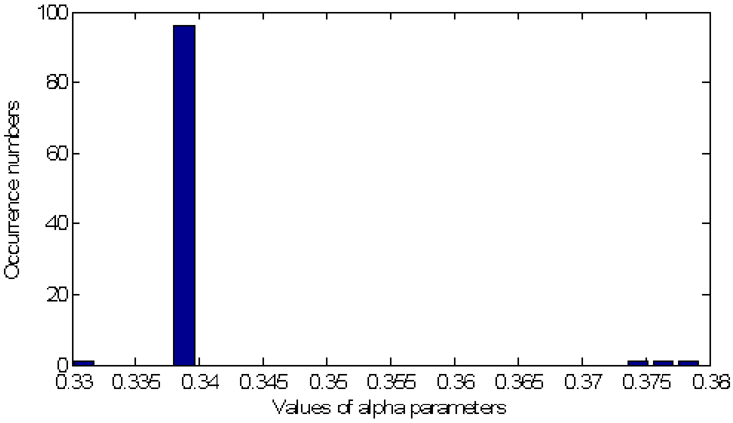

Figure 6: Occurrence number – Healthy alpha

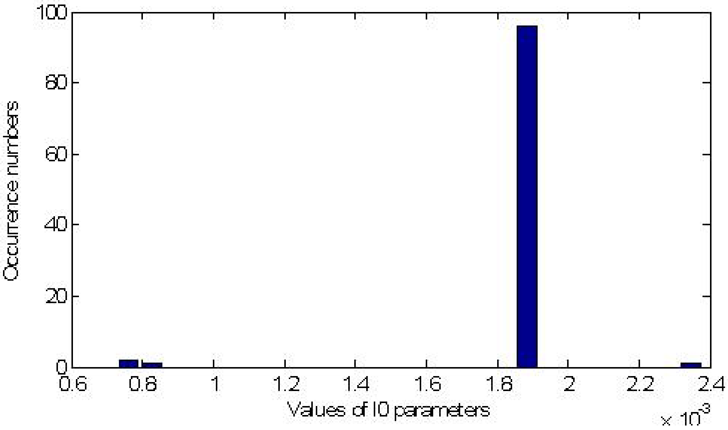

Figure 7: Occurrence number – Healthy I_0

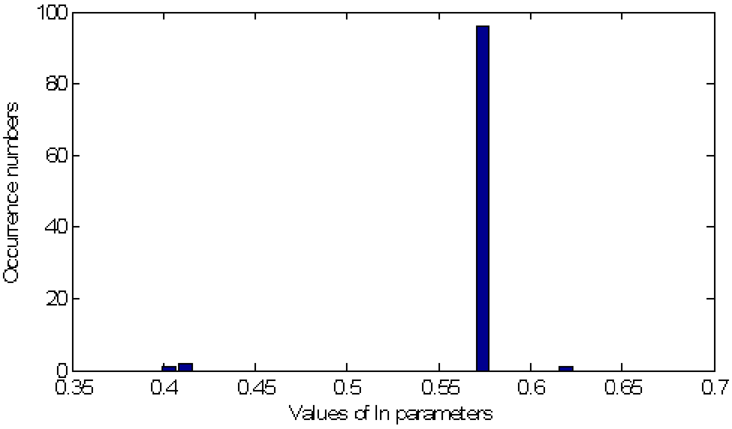

Figure 8: Occurrence number – Healthy I_n

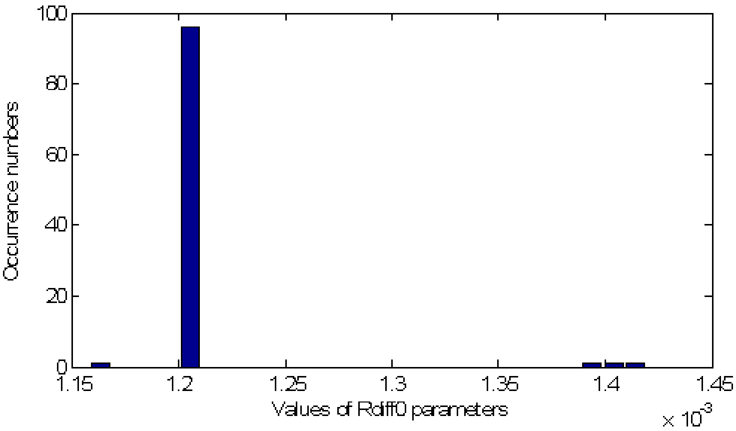

Figure 9: Occurrence number – Healthy R_{diff}

V. Application to a degraded fuel cell

Figure 10 presents the graphic of the degraded fuel cell quasi-static identification using the minimum error method and brought back to an EMC. The membrane resistance was measured to be $R_{elec\_degraded}$= 0.00155Ω. We can see that the value of the membrane resistance increased compared to the healthy value. The degradation affected the membrane which became more resistant. In addition, we can notice that a voltage drop occurred compared to the healthy case. Indeed, for I=0A, we dropped from $U_{healthy}$=0.95V to $U_{degraded}$=0.90 and this drop is amplified as we increase in current (at I=50A, $U_{healthy}$=0.64V and $U_{degraded}$=0.41).

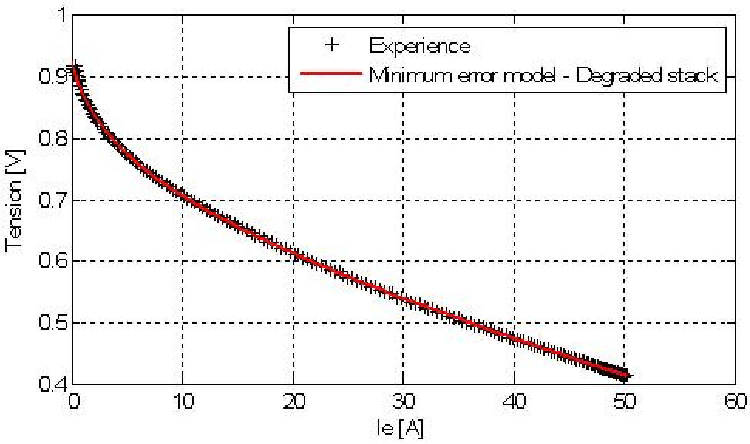

Figure 10: Quasi-static graph (EMC) – Degraded fuel cell

Table 2 presents the parameter identification results for the four unknown parameters of the quasi-static model. Again, the two selection methods are used and either of the two methods gives the same result. On the other hand, every parameter changed when compared to table 1; we will discuss about these changes in more details in the next part.

	α	I_n	I_0	R_{diff}
Min error	0.1803	1.1767	0.03893	0.002807
Max occ.	0.1803	1.1767	0.03893	0.002807

Table 2: Quasi-static identification (EMC) - Degraded fuel cell

Figure 11, 12, 13 and 14 present respectively the distribution, over the 100 optimizations, of the α, I_0, I_n and R_{diff} parameters. Again, for 95% of the achieved optimizations, the algorithm finds the same parameter value even though parameters are different from the healthy case.

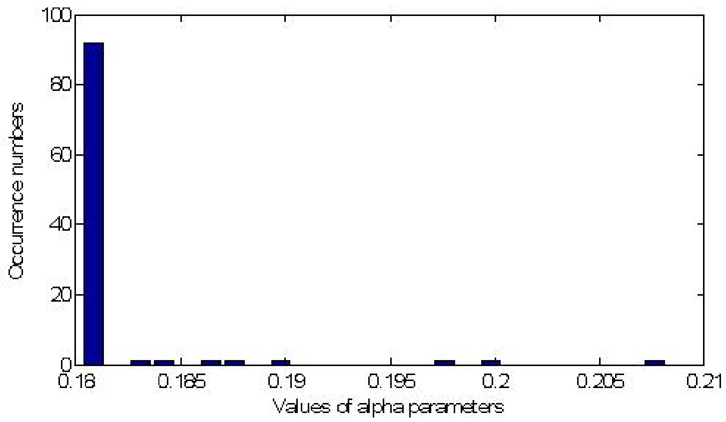

Figure 11: Occurrence number – Degraded alpha

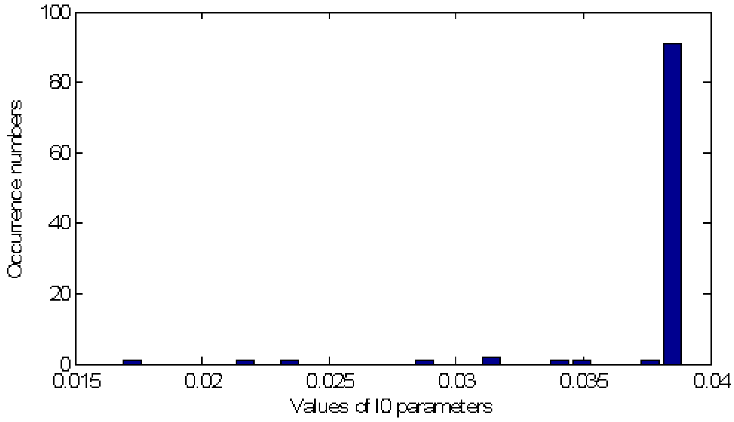

Figure 12: Occurrence number – Degraded I_0

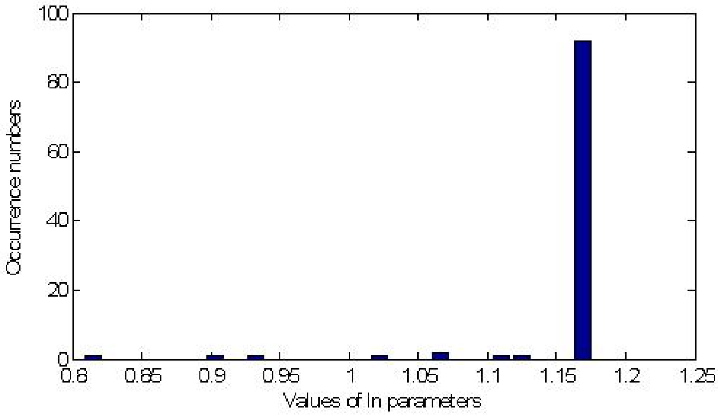

Figure 13: Occurrence number – Degraded I_n

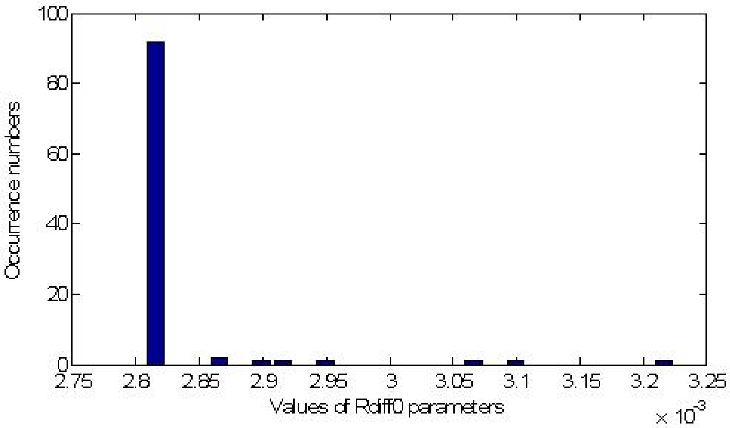

Figure 14: Occurrence number – Degraded R_{diff}

Parameters identification is now performed and thanks to the statistical method we are confident in our findings. Now, we will analyze the different losses occurring inside the fuel cell as well as their distribution (activation, diffusion, electrical). A diagnosis will be proposed based on the findings.

VI. Comparison and interpretation

The different losses, in our quasi-static model can be distributed among three categories. Equation 9, 10 and 11 present respectively the formula of the activation losses, the diffusion losses and the Ohmic losses:

$$\eta_{act} = \frac{RT}{\alpha nF} \ln\left(\frac{I + I_n}{I_0}\right) \tag{9}$$

$$\eta_{diff} = R_{diff}\, I \tag{10}$$

$$\eta_{elec} = R_{elec}\, I \tag{11}$$

In order to establish a diagnosis, healthy and degraded losses are studied. Figure 15 below presents a summary of these losses for the healthy and degraded FC. Parameters from the healthy and degraded identification are used in order to differentiate the losses (ie. $\eta_{diff\_healthy} = R_{diff\_healthy}\, I_{healthy}$).

We can observe that activation losses are predominant for both cases (healthy and degraded) and that every category of losses increased after degradation. For example, we can notice an increase of around 0.15V (0.42V to 0.57V) of the activation losses between the two states.

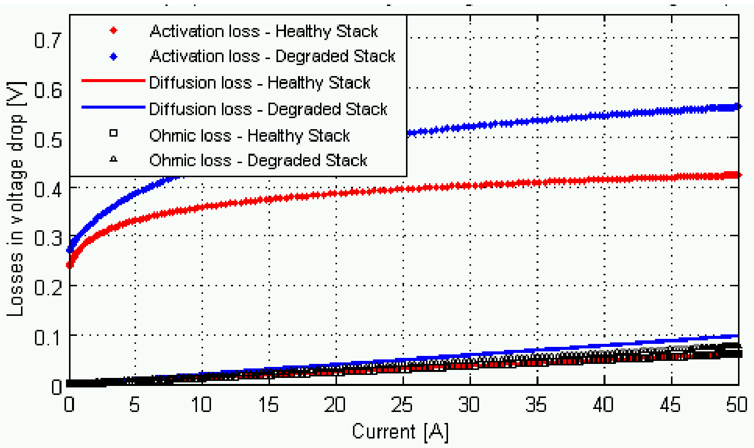

Figure 15: Comparison of healthy and degraded fuel cell losses - Voltage drop

Figure 16 presents the losses brought back to a percentage loss of E_{rev}. This representation allow us to observe that for example, at 50A, activation losses represents around 47% of the E_{rev} for the degraded model for around 36% for the healthy one.

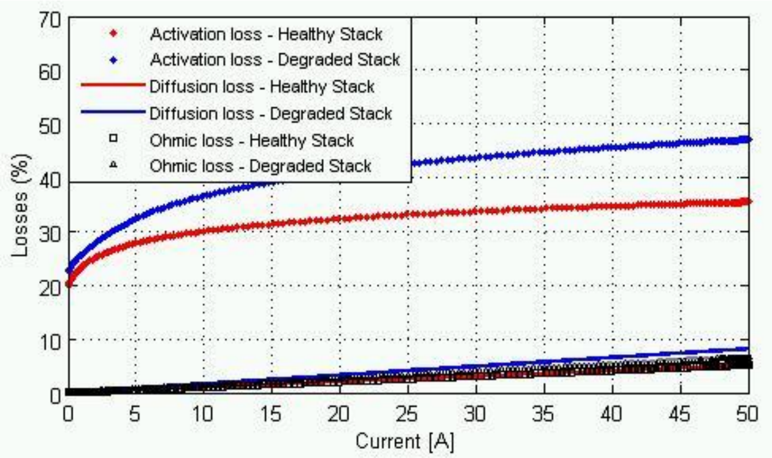

Figure 16: Comparison of healthy and degraded fuel cell losses – Percentage of E_{rev}

Finally, figure 17 introduces new information, the deterioration with respect to the healthy state and equation 10 presents the relation used to produce this graphic.

$$Deterioration\,(\%) = \frac{|Healthy - Degraded|}{Healthy} * 100 \quad (10)$$

This last figure allows us to determine which quantity has been the most damaged. We can observe that, even though activation losses represent half of the losses, the most important degradation is taking place at the diffusion level. Indeed, we can see in figure 17 that the diffusion deterioration with respect to the healthy state is around 60%. The degradation for the activation and Ohmic resistance is lower as we have respectively a 32% and 26% drop in performance.

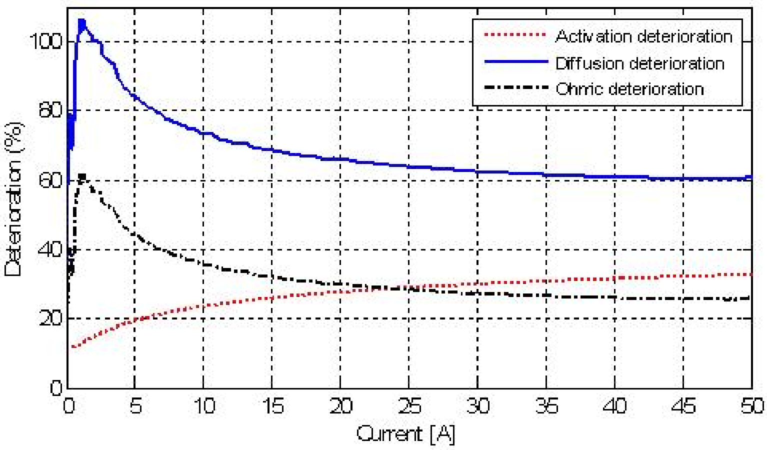

Figure 17: Deterioration with respect to the healthy state in percentage

VII. Conclusion

In this paper, physicochemical parameters identification has been performed on a quasi-static circuit–based model. This method could be useful for transportation applications. Indeed, the identified parameters allow the estimation of the different losses occurring within the FC. From these estimations we can extract relevant information regarding the fuel cell state of health in order to favor predictive maintenance operations and decide on the fuel cell optimal control for the improvement of the fuel cell life time.

The identification process shows that final solutions differ depending on the algorithm starting point. The statistical parameters repartition underlines recurrent parameter values. The solution with the most recurrent parameter values correspond to the solution extracted using the minimum error method. For future tests, the minimum error method will be kept as it is easier to implement and it provides more accurate results with a good confidence index.

Today, all these approaches are also applied to parameters identification of dynamic models of a PEM fuel cell and PEM electrolyzer.

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